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## ON THE CAPACITY OF A LEAD STORAGE CELL.

By MASAO KUBOKAWA.

### Introduction.

The capacity of a lead storage cell is influenced by various factors: (1) the end-point voltage of discharge, (2) the character of plates, such as their surface area, thickness, and porosity, (3) the concentration of sulphuric acid and its amount, (4) the rate of discharge, (5) the temperature, etc. It is, therefore, very hard theoretically to calculate the capacity of the cell or design it for an expected capacity. Makers design their cells solely from their experience of long years and a sufficient theoretical ground is desired as the basis of the design.

Many formulae have been presented in which one or two of the factors affecting the capacity of the cell are regarded as variables and the others as constants. The relation between the rate of discharge and the capacity, above all, has been studied so much that there are many formulae proposed for it. The constants adopted, however, lack much physical meaning and accompany the inconvenience of having to be determined experimentally one by one. Recently a theoretical equation was proposed by Tiku,<sup>1)</sup> but how far it is practically applicable is not made public. The discharge is such a complicated phenomenon that there are many problems still unanswered with regard to it. When we treat the discharge theoretically, it is necessary to make many hypotheses. The present author, dealing with the problem as simply as possible, has reached an equation by which the capacity can be readily obtained by calculation. He intends to make it more complete by comparing the value calculated by it with that measured. In this first report, there will be stated the manner of leading out this simple equation and the comparison made between the measured and calculated values of the capacity for the positive and negative plates of various thicknesses.

### Theoretical.

#### On the end-point of discharge.

The capacity of a cell is generally represented by the product (Ahr) of the current and the time taken by the terminal voltage to reach a certain end-point.

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1) Tiku, *Bull. Toyoda Research Imp. Invention Soc. Japan*, 3, 99 (1935): 5, 56 (1938).

The end-point is empirically fixed by makers lest the life of the cell should be injured, and so the capacity is fairly variable according to the manner of determining the end-point.<sup>2)</sup> The end-point or whatever are closely related to it must be regarded as variables in the equations indicating the capacity.

After the end-point in the above sense is reached, the terminal voltage drops rapidly. In order to deal with the capacity theoretically, it is necessary to consider the reason why the voltage drops rapidly. In the lead storage cell the active material of the positive plate is made of lead dioxide and that of negative plate is made of sponge lead, these active materials of the pasted plates being very porous. According to the double sulphate theory the sulphuric acid filling those pores becomes fixed as lead sulphate by discharge and accordingly its concentration diminishes gradually. Hence the concentration polarisation takes place and the voltage drops. Not only the resistance of sulphuric acid increases more and more, but also the lead sulphate formed is a material having a high resistance. Therefore the polarisation caused by the decrease of sulphuric acid and the increase of the internal resistance are regarded as the causes of the rapid drop of voltage at the end-point of discharge. Let  $V$  represent the terminal voltage during discharge,  $E$  the electromotive force,  $i$  the current, and  $R$  the internal resistance, and we have

$$V = E - i \cdot R$$

According to an actual measurement,  $R$  increases during discharge and at the positive plate it is ten times as high as at the negative plate, but the value is in the order of  $10^{-2} \Omega$ .<sup>3)</sup> It is, therefore, not to be inferred that the rapid drop of  $V$  is due to  $R$ .  $E$  is the electromotive force at the state of the concentration polarisation. It is already known that the potential of the positive plate which constitutes  $E$  drops rapidly with the decrease of concentration of sulphuric acid after passing a certain point.<sup>4)</sup> So far as the positive plate is concerned, the end-point of discharge seems to be caused by the polarisation which is due to the decrease of the concentration of the sulphuric acid on the surface of the active material. This inference is supported by the fact that when sulphuric acid is forced to diffuse through the plate by gravitation, the capacity increases,<sup>5)</sup> or that if a cell is left unused for a while after its voltage has been reduced to

2) For example, Lyndon, "Storage Battery Engineering" (1911) p. 91.

3) Matsumoto, *J. Electrochem. Assoc. Japan*, 4, 464 (1936).

4) Harned and Hamer, *J. Am. Chem. Soc.*, 57, 27 (1935).

5) Liebenow, *Z. Elektrochem.*, 4, 61 (1897).

Tiku, *Bull. Toyoda Research Imp. Invention Soc. Japan*, 2, 49 (1934).

the end at a high rate of discharge, it becomes capable of being discharged again.<sup>6)</sup>

If the end-point of discharge is ascribed to the decrease of the concentration of the sulphuric acid in the pores, the rates of consumption and supply of sulphuric acid must be taken into account. Let  $v_e$  represent the rate at which the sulphuric acid in the pores is consumed during discharge,  $v_s$  the rate at which it forms lead sulphate by self-discharge (not by discharge), and  $v_d$  the rate at which it diffuses into the pores from the outside of the plate. Then, in accordance with current strength, there may be the following two cases, where the concentration of the sulphuric acid in the pores is remarkably different from each other in the end.

(1)  $v_e + v_s > v_d$  ..... discharge at high rates.

(2)  $v_e + v_s \leq v_d$  ..... discharge at low rates.

In the case of high rates of discharge, the concentration of the sulphuric acid in the pores becomes smaller with the progress of the discharge and at last approaches zero. Thus, though the active material remains unacted, the discharge may become impossible. On the other hand, in the case of (2), low rates of discharge, sulphuric acid is sufficiently supplied from the outside of the pores so that the active material would be completely covered with lead sulphate at length unless its diffusion is obstructed. In this case the discharge will be impossible all the same in spite of sufficient existence of sulphuric acid in the pores. Even in such a case, if the cross-section of the pores diminished gradually, as Dolezalek thought, or if the stream line of the current penetrated deep into the pores with the progress of the discharge<sup>7)</sup>, then the diffusion of the sulphuric acid would be checked and the end-point would come owing to the lack of the sulphuric acid similarly as in the case (1). As the rate of self-discharge  $v_s$  is fairly high when the concentration of sulphuric acid is large or its temperature is high, it cannot be properly neglected in the case (2) as in the case (1) where  $v_e$  is high.

In the present paper, the comparatively simpler case (1) of the capacity at discharge at high rates will be taken up first.  $v_s$  is negligible in comparison with  $v_e$  and, for the sake of briefness, the dimension of the pores is assumed as unchangeable during the discharge.

#### Kinetics of the discharge at high rates.

A cell is constructed by setting a plate between two anti-plates of higher

6) Tiku, *ibid.*, 6, 27 (1939).

7) Dolezalek, "Die Theorie des Akkumulators" 90 (1901).

capacity; the capacity of the cell is controlled by the central plate. The plates are soaked in a sufficient quantity of dilute sulphuric acid whose concentration  $c_0$  (mol/cm<sup>3</sup>) is assumed to be unchangeable during discharge. The active material of a pasted plate is extremely porous and innumerable capillaries are assumed to fill the plate. But assume here, for briefness' sake, that those capillaries are all cylindrical in shape and equal in dimensions, and are arranged at right angles to the surface of the plate. Let  $q$  (cm<sup>2</sup>) represent the cross-section of a capillary and  $l$  (cm) its length.

Let us assume that the concentration of the sulphuric acid filling the capillaries diminishes linearly towards the interior of the pores during discharge. Represent the concentration gradient at the entrance of the pores by  $dc/dx$ , then  $ds$ , the amount of the sulphuric acid, which diffuses into the pores during the time  $dt$ , can be determined from Fick's law as follows:

$$ds = -Dq \left( \frac{dc}{dx} \right) dt \quad (1)$$

where  $D$  is the diffusion coefficient (cm<sup>2</sup>/hr) of sulphuric acid. If the concentration of the sulphuric acid at the bottom of the pores is represented by  $c_m$ , then  $-\left(\frac{dc}{dx}\right) = \frac{c_0 - c_m}{l}$  and  $c_m = \frac{c_0 + c_e}{2}$ , where  $c_m$  is the mean concentration in the pores. Assuming that on the whole surfaces of the plate there are  $n$  pores whose total volume is  $v$  (cm<sup>3</sup>),  $nds = vdc$  and  $v = nql$ . By substituting these values in equation (1) the rate at which the concentration of sulphuric acid increases by diffusion into the plate is given as follows:

$$+ \left( \frac{dc}{dt} \right) = \frac{2D}{l^2} (c_0 - c_m) \quad (2)$$

On the other hand, the rate at which the concentration of sulphuric acid diminishes by the discharge ( $iA$ ) is expressed as follows:

$$- \left( \frac{dc}{dt} \right) = \frac{m}{v} \cdot i \quad (3)$$

where  $m$  is the number of gram mol (mol/A hr) of the sulphuric acid which is diminished during the discharge per 1 A hr. The value is obtained from the double sulphate theory with correction made by the transport number. The details will be taken up later.

In practice, the concentration of the sulphuric acid in the pores is diminished by the difference between the rate of consumption (3) and that of supply (2). Hence the following differential equation:

$$-\frac{dc_m}{dt} = \frac{m}{v} i - \frac{2D}{l^2} (c_o - c_m). \quad (4)$$

By integration, it becomes as follows:

$$-\frac{l^2}{2D} \left[ \frac{2D}{l^2} (c_o - c_m) - \frac{m}{v} i \right] = t - \text{const.}$$

When  $t=0$ ,  $c_m=c_o$ . By substituting the integration constant obtained:

$$-\ln \left[ 1 - \frac{2Dv}{ml^2i} (c_o - c_m) \right] = \frac{2Dt}{l^2} \quad (5)$$

Let  $K$  represent capacity. By substituting  $K=it$  and using common logarithms, the following equation of capacity is obtained:

$$K = -\frac{l^2 i}{0.868 D} \log \left[ 1 - \frac{2Dv}{ml^2i} (c_o - c_m) \right]. \quad (6)$$

By expanding equation (5) for simplicity's sake:

$$K = -\frac{l^2 i}{2D} \left[ -\frac{a}{i} - \frac{1}{2} \left( \frac{a}{i} \right)^2 - \frac{1}{3} \left( \frac{a}{i} \right)^3 - \dots \right]$$

where  $a \equiv \frac{2Dv}{ml^2} (c_o - c_m)$ . If  $i$  is much higher than  $a$ , the terms higher than square may be omitted. Thus the equation sought after becomes as follows:

$$K = \frac{v(c_o - c_m)}{m} + \frac{Dv^2(c_o - c_m)^2}{m^2 l^2 i} \quad (7)$$

Equation (7) is different from that of Tiku<sup>8)</sup> merely in constants.

The mean length of the capillaries is unknown at present, but the most probable value will be obtained by assuming  $1/2$  of  $d$  (cm), the thickness of a plate, to be equal to  $l$ :

$$K = \frac{v(c_o - c_m)}{m} + \frac{4Dv^2(c_o - c_m)^2}{m^2 d^2 i}. \quad (8)$$

Let us compare the value of  $K$  obtained by calculating the right-hand side of equation (8) with the capacity measured. In the right-hand side of (8),  $v$ ,  $d$ ,  $c_o$ , and  $i$  can be readily measured, but  $D$ ,  $m$ , and  $c_m$  must be found out.

**The value of  $D$ :**—The value of  $D$ , the diffusion coefficient of sulphuric acid, has been measured by a few investigators at low temperatures.<sup>9)</sup> Assuming temperature coefficient of  $D$  to have no relation to the concentration and

8) Tiku, *Bull. Toyoda Research Imp. Invention Soc. Japan*, 5, 59 (1938).

9) Landolt, "Tabellen" (1) 248 (1923).

concentration and extrapolating from the value at 18°C., the equation demanded becomes :

$$D = 0.0538 + 9.04c + 0.00133(T - 18) \quad (9)$$

where  $D$ ,  $c$ , and  $T$  are expressed in  $\text{cm}^2/\text{hr}$ ,  $\text{mol}/\text{cm}^3$ , and Centigrade respectively. As the concentration of the sulphuric acid in the pores diminishes with the progress of the time, the mean value of  $c_0$  and  $c_m$  is used as the value of  $c$ .

**The value of  $m$  :—** The result obtained by Dolezalek<sup>10)</sup> is adopted as  $m$  the number of mol of the sulphuric acid which diminishes during the discharge per 1 A hr. Let  $\mu$  represent the transport number of hydrogen ion. During the discharge of  $2F$ ,  $\mu$  mol of sulphuric acid are consumed at the negative plate while at the positive plate  $(2 - \mu)$  mol of it are consumed and 2 mol of water are generated. If 0.81 is adopted as the value of  $\mu$  for 20 % sulphuric acid, the result is that 0.81 mol of sulphuric acid diminishes at the negative plate and 1.28 mol at the positive. Converting those values for 1 A hr, we have

$$\begin{aligned} m &= 0.0239 \text{ mol/Ahr.....for pos. plate.} \\ m &= 0.0151 \text{ mol/Ahr.....for neg. plate.} \end{aligned} \quad (10)$$

By neglecting the fact that the value of  $\mu$  is more or less variable with temperature and concentration, the above value is adopted for  $m$ .

**The value of  $c_m$  :—**  $c_m$  the mean concentration of the sulphuric acid in the pores during discharge is assumed to be regularly related to the terminal voltage. If this relation is made clear,  $c_m$  will be directly known from the value of the end-point voltage. Reserving the matter for future studies, here  $c_m$  is assumed to be concentration of the sulphuric acid of sp. g. 1.05 when the end-point voltage is 1.70 V. This value of sp. g. is based on the data of Earle<sup>11)</sup> when he measured the capacity for the non-porous plate of Chloride type soaked in sulphuric acid of various specific gravities with weak current. Extrapolating the curve of the mean terminal voltages obtained by him during discharge, it is known that 1.70 V generally corresponds to sp. g. 1.05. Assuming that this relation is not influenced by the rate of discharge and thickness of the plate, when the end-point voltage is 1.70 V,  $c_m$  becomes :

$$c_m = 0.786 \times 10^{-3} \text{ mol}/\text{cm}^3. \quad (11)$$

### Experimental.

**Method.** Generally speaking, the capacity of a plate varies gradually by

10) Dolezalek, *loc. cit.* s. 68.

11) Earle, *Z. Elektrochem.*, 2, 519. (1895-6).

repetition of charges and discharges, and so an exact relation between current and capacity can not be known from the same plate. Assuming, therefore, the plates made under the same condition to be the same in quality, the relation was made out by discharging each of the plates by a different current. To know the influence of the thickness of the plate, six kinds of positive plates to be experimented with different currents, six kinds of positive plates of different thicknesses, six kinds of negative plates for different currents, and seven kinds of negative plates for different currents, and seven kinds of negative plates of different thicknesses—78 plates in total—were used in the present experiment.

For measuring capacity, the cells with test plates, connected in series in order of thickness of the plates, discharged with a current regulated by a sliding resistance. As the cells reach the end-point in order of their capacity, switches were inserted to cut off such cells at once from the circuit. Sometimes a desired current could not be got from the test cells only, and a direct current source of 110 V was applied to the circuit.

The terminal voltage of each cell was measured every five minutes during discharge, and every one minute when the voltage of the cell was near to its end-point. In the following experiments the end-point voltage was fixed at 1.70V. Measurement of voltage for the cadmium auxiliary electrode was also made in parallel with that of the terminal voltage and it was ascertained that the capacity was absolutely controlled by the test plates.

The charge was made by 0.5 A for 38 hr for the positive test plates, and by 1.0 A for 50 hr for the negative plates. The measurement of capacity was begun 3 hr after completion of the charge.

The specific gravity of dilute sulphuric acid used to fill the cells was 1.210 (30°C./4°C.) and each cell required 3.4 L of it. The sp. g. was hardly varied by discharge, the greatest difference being only 0.005, and so this difference was neglected from calculation.

All the test cells were placed in a thermostat and always kept at  $30^{\circ} \pm 0.5^{\circ}\text{C}$ . throughout the measurements.

**Test Plates.** The grids of the AV Type made of alloy of lead and antimony were used in layers of one to seven sheets. Each sheet was 0.15 cm in thickness and  $9.7\text{ cm} \times 10.3\text{ cm} \div 100\text{ cm}^2$  in area. It had also thin cross bars: fourteen lengthwise and five breadthwise. These grids were made by piling up the sheets needed, and their edges were perfectly burned by flame.

The paste applied to the above grids was a special one made tentatively.



The same paste was employed for both positive and negative plates. The paste was a mixture of 300 g of yellow lead monoxide powder and 56 cc sulphuric acid of sp. g. 1.10. The grid applied with this paste was dried with caution not to allow it to crack, and was formed with 1.0 A in dilute sulphuric acid of 1.05 sp. g. The time of formation was 37~252 hr according to the thickness of the plates. As the same paste was used for both positive and negative plates, the latter came to have larger porosity, as will be mentioned later.

The volume,  $v$ , of the pores in the plate was measured in the following manner. A plate of a known capacity was taken out after the charge, freed from sulphuric acid by washing, and dried rapidly in a vacuum desiccator with a heater. The volumes of the active materials ( $v_a$ ) were calculated, after subtracting the weight of the grid from that of the dried plate, with the figures 11.34 and 8.92 for the densities of the active materials of the negative and positive plates.<sup>12)</sup> They were assumed to be composed of pure Pb and PbO<sub>2</sub>. The apparent volume of the active material ( $v + v_a$ ) can be obtained by subtracting the volume of the grid from that of the plate.<sup>13)</sup> The porosity of the plate  $p$  is expressed by  $\left(\frac{v}{v + v_a}\right) \times 100$ , which will be noted in each datum for reference's sake.

The anti-plates to be combined with the test plates must be sufficiently large in capacity. In the present experiment the plates of MT Type were used. The negative plates were of the passed type of 15.1 cm  $\times$  15.5 cm  $\times$  0.4 cm and the positive plates were of Tudor plates of 15.1 cm  $\times$  15.3 cm  $\times$  0.9 cm.

#### Results of the experiments on the positive plates of various thicknesses.

The relation between the capacity measured by various current strength and the thickness of the plates is shown in Fig. 1.

The difference  $\Delta K$  between  $K'$  the capacity measured and  $K$  the capacity obtained from equation (8) is tabulated in the following table, where thickness of the plates  $d$  (cm), volume of the pores  $v$  (cm<sup>3</sup>), and porosity  $p$  (%) are the mean values for six plates respectively. Values of  $D$ ,  $m$ ,  $c_p$ , and  $c_m$  to be substituted in the theoretical equation (8) were taken as follows:

12) Kinoshita, *Bull. Toyoda Research Imp. Invention Soc. Japan*, 1, 53 (1932).

13) Tiku, *ibid.*, 5, 66 (1938).

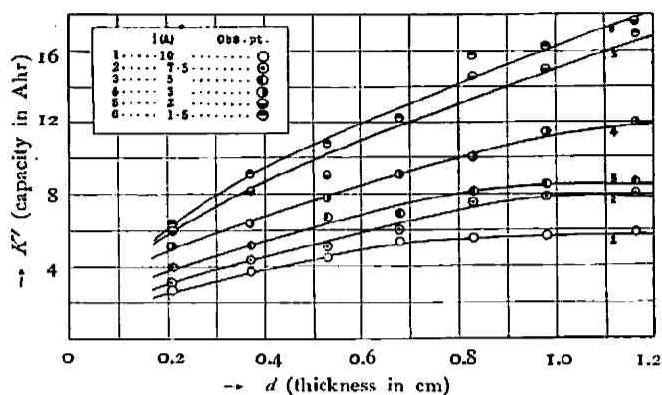


Fig. 1. Positive plates.

$D=0.0900 \text{ cm}^2/\text{hr}$ ,  $m=0.0239 \text{ mol/Ahr}$ ,  $c_o=3.70 \times 10^{-3} \text{ mol/cm}^3$ ,  $c_m=0.786 \times 10^{-3} \text{ mol/cm}^3$ .

Table 1. Capacity of positive plates.

(1)  $d=0.210 \text{ cm}$ ,  $v=10.76 \text{ cm}^3$ ,  $p=60.6\%$ 

$i$ (A)	$K'$ (obs.)	$K'$ (calc.)	$\Delta K'$
10.0	2.67	2.72	-0.05
7.5	3.12	3.19	-0.07
5.0	3.92	4.13	-0.21
3.0	5.15	5.50	-0.35
2.0	6.00	8.36	-2.36
1.5	6.38	10.69	-4.31

(2)  $d=0.375 \text{ cm}$ ,  $v=18.20 \text{ cm}^3$ ,  $p=59.7\%$ 

$i$ (A)	$K'$ (obs.)	$K'$ (calc.)	$\Delta K'$
10.0	3.66	3.48	+0.18
7.5	4.38	3.91	+0.47
5.0	5.16	4.75	+0.41
3.0	6.41	6.44	-0.03
2.0	8.16	8.55	-0.39
1.5	9.16	10.66	-1.60

(3)  $d=0.534 \text{ cm}$ ,  $v=25.26 \text{ cm}^3$ ,  $p=58.5\%$ 

$i$ (A)	$K'$ (obs.)	$K'$ (calc.)	$\Delta K'$
10.0	4.50	4.28	+0.22
7.5	5.12	4.69	+0.43
5.0	6.67	5.49	+1.18
3.0	7.75	7.10	+0.65
2.0	9.00	9.10	-0.10
1.5	10.79	11.10	-0.31

(4)  $d=0.682 \text{ cm}$ ,  $v=32.31 \text{ cm}^3$ ,  $p=58.0\%$ 

$i$ (A)	$K'$ (obs.)	$K'$ (calc.)	$\Delta K'$
10.0	5.34	5.14	+0.20
7.5	6.13	5.55	+0.58
5.0	6.91	6.35	+0.56
3.0	9.05	7.96	+1.09
2.0	13.91*	9.96	—
1.5	12.25	11.98	+0.27

(5)  $d=0.831 \text{ cm}$ ,  $v=38.16 \text{ cm}^3$ ,  $p=57.3\%$ 

$i$ (A)	$K'$ (obs.)	$K'$ (calc.)	$\Delta K'$
10.0	5.50	5.78	-0.28
7.5	7.50	6.16	+1.34
5.0	8.16	6.91	+1.25
3.0	10.00	8.40	+1.60
2.0	14.56	10.30	+4.26
1.5	15.75	12.14	+3.61

(6)  $d=0.979 \text{ cm}$ ,  $v=46.62 \text{ cm}^3$ ,  $p=58.0\%$ 

$i$ (A)	$K'$ (obs.)	$K'$ (calc.)	$\Delta K'$
10.0	5.66	6.91	-1.25
7.5	7.75	7.31	+0.41
5.0	8.51	8.12	+0.39
3.0	11.40	9.74	+1.66
2.0	14.95	11.77	+3.18
1.5	16.22	13.79	+2.43

\* This large value is due to the existence of a blister on the surface of the plate.

The relation between  $K$  and  $1/i$  is given in Fig. 2. The deviation of the point of the measured capacity from the theoretical line is extremely large when

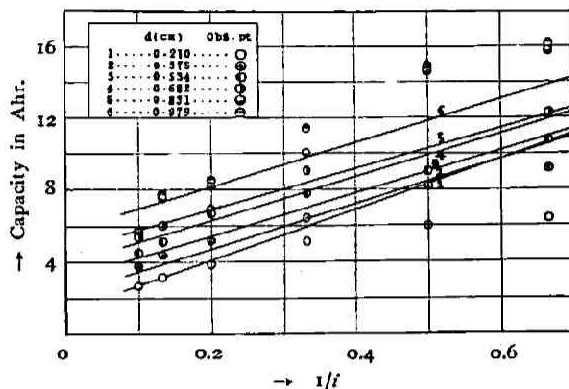


Fig. 2. Positive plates.

$1/i$  is large, that is, in the case of discharge at low rates, and likewise when the thickness of the plates  $d$  is small. But within some range both agree well.

### Results of the experiments on negative plates of various thicknesses.

The results of measurements on the negative plates is shown in Fig. 3.

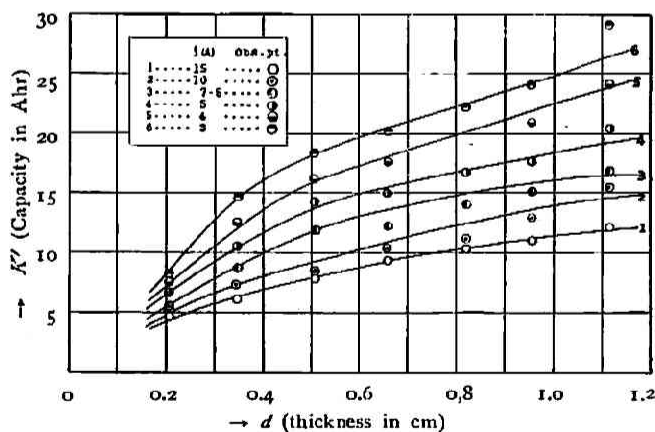


Fig. 3. Negative plates.

The comparison between  $K$ , the capacity calculated from equation (8), and  $K'$ , the capacity measured, is tabulated in Table 2. Values of  $D$ ,  $\epsilon_0$  and  $\epsilon_m$  used for calculation were the same as in the case of positive plates. For the value of  $m$ , however,  $m=0.0151$  mol/Ahr was adopted from equation (10).

Table 2. Capacity of negative plates.

(1)  $d=0.209$  cm,  $v=12.97\text{cm}^3$ ,  $p=72.8\%$ 

$i$ (A)	$K'$ (obs.)	$K''$ (calc.)	$\Delta K''$
15.0	4.68	5.95	-1.27
10.0	5.18	7.68	-2.50
7.5	5.50	9.40	-3.90
5.0	6.70	12.85	-6.15
4.0	7.50	15.45	-7.95
3.0	8.20	19.75	-11.55

(2)  $d=0.348$  cm,  $v=20.40\text{cm}^3$ ,  $p=71.2\%$ 

$i$ (A)	$K'$ (obs.)	$K''$ (calc.)	$\Delta K''$
15.0	6.15	7.02	-0.87
10.0	7.35	8.55	-1.20
7.5	8.70	10.10	-1.40
5.0	10.50	13.19	-2.69
4.0	12.50	15.49	-2.99
3.0	14.70	19.34	-4.64

(3)  $d=0.508$  cm,  $v=29.13\text{cm}^3$ ,  $p=70.4\%$ 

$i$ (A)	$K'$ (obs.)	$K''$ (calc.)	$\Delta K''$
15.0	7.83	8.56	-0.73
10.0	8.50	10.03	-1.53
7.5	11.90	11.51	+0.39
5.0	14.25	14.44	-0.19
4.0	16.10	16.63	-0.53
3.0	18.40	20.32	-1.92

(4)  $d=0.661$  cm,  $v=37.09\text{cm}^3$ ,  $p=69.7\%$ 

$i$ (A)	$K'$ (obs.)	$K''$ (calc.)	$\Delta K''$
15.0	9.35	9.97	-0.62
10.0	10.40	11.38	-0.98
7.5	12.20	12.79	-0.59
5.0	15.00	15.60	-0.60
4.0	17.60	17.71	-0.11
3.0	20.20	21.21	-1.01

(5)  $d=0.821$  cm,  $v=44.49\text{cm}^3$ ,  $p=69.1\%$ 

$i$ (A)	$K'$ (obs.)	$K''$ (calc.)	$\Delta K''$
15.0	10.38	11.21	-0.83
10.0	11.20	12.53	-1.33
7.5	14.00	13.84	+0.16
5.0	16.75	16.47	+0.28
4.0	—	18.44	—
3.0	22.30	21.70	+1.00

(6)  $d=0.960$  cm,  $v=52.10\text{cm}^3$ ,  $p=69.0\%$ 

$i$ (A)	$K'$ (obs.)	$K''$ (calc.)	$\Delta K''$
15.0	11.00	12.69	-1.69
10.0	12.90	14.00	-1.10
7.5	15.05	15.32	-0.27
5.0	17.63	17.95	-0.32
4.0	20.95	19.93	+1.02
3.0	24.10	23.23	+0.87

(7)  $d=1.117$  cm,  $v=62.11\text{cm}^3$ ,  $p=70.5\%$ 

$i$ (A)	$K'$ (obs.)	$K''$ (calc.)	$\Delta K''$
15.0	12.10	14.75	-2.65
10.0	14.50	16.14	-1.64
7.5	16.85	17.51	-0.66
5.0	20.40	20.28	+0.12
4.0	24.05	22.34	+1.71
3.0	29.10	25.71	+3.31

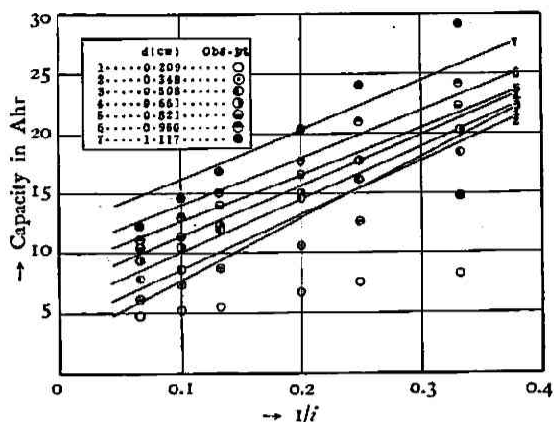


Fig. 4 Negative plates.

The relation between  $K$  and  $1/i$  is shown in Fig. 4. The deviation of the point of the measured capacity from the theoretical line is exceedingly large when the plates are thin, but both agree well at a certain thickness of the plates.

#### Discussion of Results.

Though equation (8) mentioned in the theoretical part was derived from an extremely simple assumption, the capacity calculated from that equation and that obtained from actual measurements agree not only in order but in a certain range of thickness of the plates and of current strength. This fact indicates that the assumption is quite near to truth within a certain limit.

On the other hand, the deviation is fairly recognizable; if the positive plates are thinner the calculated value is larger than the measured value and this difference grows larger at discharge at low rates. Such a tendency appears more remarkably at the negative plates than at the positive. On the contrary, when the plates are thick beyond a certain degree, the tendency becomes reverse and the calculated value is smaller than the measured value. The lower the current is, the larger the difference is.

In the case of discharge at low rates the calculated capacity does not agree with that measured. This is, however, natural, because equation (8) was led for the case of discharge at high rates. For the case of discharge at low rates its end-point must be considered differently.

The deviation occurring when the plates are markedly thin or markedly thick seems to be due to the assumptions for the dimension of the pores and for the rate of diffusion.

The pores are really not cylindrical but complicated and winding in shape, and their mean length is probably larger than  $1/2$  of the thickness of the plates. This fact may cause the deviation seen in the case of thin plates. On the contrary, when the plates are too thick, it is difficult for sulphuric acid to diffuse as far as the bottom of the pores, and there is an effect brought about as if the pores were shorter.

It was assumed that the concentration gradient of sulphuric acid is linear, but it is questionable, too. It has been much discussed whether lead sulphate begins to be formed at the entrance of the pores or at their bottom during discharge.<sup>14)</sup> In the present report it is assumed that lead sulphate is always first formed at both positive and negative plates at the bottom of the pores. The matter must be studied further. Although the cross-section of the pores was regarded as constant, it was found out that it was often reduced to about  $1/2$  of its original section owing to the lead sulphate formed at discharge.<sup>15)</sup> It seems, therefore, to be incorrect unless Dolezalek's theory<sup>16)</sup> is adopted for it, according to which the cross-section of the pores becomes smaller according as the time goes on.

Fick's law has been said not to be strictly applicable to such an electrolyte as sulphuric acid, especially in the case where its concentration gradient is large. All these facts seem to be the causes of the deviations above mentioned. Finally, the foundation by which the mean concentration of sulphuric acid was obtained from the terminal voltage is theoretically not certain. It is desirable to obtain a more complete equation by solving the above questions.

### Summary.

- 1) The end-point of discharge of a lead storage cell has been considered.
- 2) By forming simple hypotheses, the capacities at high rates of discharge have been theoretically dealt with and an equation has been obtained.
- 3) In order to compare the theory with the practice, the capacities of the positive and negative plates of various thicknesses have been measured with the sulphuric acid of 1.210 sp. g. at 30°C. at various rates of discharge.
- 4) It has been ascertained that the calculated capacity agrees with the measured capacity in the case of the positive plates of 3~8 mm in thickness at

14) Tiku, *Bull. Toyoda Research Imp. Invention Soc. Japan*, 6, 33 (1939).

15) Kubokawa, The details have not been made public yet.

16) Dolezalek, *Loc. cit.*, s. 90.

discharge at high rates of more than  $1.5 \text{ A/dm}^2$  and also in the case of the negative plates 5~10 mm in thickness at discharge at high rates of more than  $3 \text{ A/dm}^2$ .

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